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(54) Title: NON-ZEOLITIC NANOCOMPOSITE MATERIALS FOR SOLID ACID CATALYSIS

(57) Abstract: One aspect of the present invention relates to a catalytic compound of anion-modified metal oxides doped with metal ions. Another aspect of the present invention relates to a method of isomerizing an alkane or alkyl moiety.

**NON-ZEOLITIC NANOCOMPOSITE MATERIALS
FOR SOLID ACID CATALYSIS**

Background of the Invention

5 Heterogeneous catalysis has played a critical role in many chemical processes. The impact of heterogeneously catalyzed processes on the global economy has been estimated at 20% of the world GNP, i.e., roughly \$5 trillion/year. The main industrial applications of heterogeneous catalysis are petroleum refining, chemical production, and environmental protection. Petroleum refining involves the largest volume of materials processed, with the
10 world oil refining capacity in excess of 3.6×10^{12} kg/year.

Acid catalysis forms the basis of the most highly utilized hydrocarbon conversion processes in the petroleum industry, and constitutes an active field of research today. Although the industrial processes, such as paraffin isomerization, alkylation, catalytic cracking, and naphtha reforming, lead to different end-products, they all depend on
15 materials with surface acidity. Environmental problems with the upstream of the refined hydrocarbon products have goaded the search for improved acid catalysts. In the production of motor-grade fuel through alkylation of isobutane with alkenes, H₂SO₄ or HF is used as the catalyst. These liquid mineral acids are corrosive, dangerous to handle, and difficult to dispose of. Even some industrial solid acid catalysts are environmentally
20 harmful. For example, the bifunctional Pt-doped chlorinated alumina catalyst used in the n-butane isomerization process requires the addition of chlorinated compounds to maintain catalytic activity because it leaches corrosive HCl during use.

More significant are the problems concerning the downstream use of the hydrocarbon products, especially the deleterious emissions from the combustion of gasoline
25 motor fuel. Addressing this was the Clean Air Act Amendments of 1990, which mandated the reformulation of motor fuel gasoline (40-50% of all petroleum products in the US). As a result, demand for particular blend components has heightened, increasing the load on existing catalytic processes. Aluminosilicate zeolites have attempted to address these environmental issues, but there is much more room for improvement, given the
30 development of novel solid acidic materials.

Aluminosilicate zeolites are microporous, crystalline materials composed of AlO₄ and SiO₄ tetrahedra arranged around highly ordered channels and/or cavities. Zeolites are acidic solids, in which the surface acidity is generated by protons required for charge

balance of the framework and located near the Al cations. More generally referred to as molecular sieves, these materials have structural properties desirable for solid acid catalysts, such as surface acidity, high surface areas, and uniform pore sizes. Examples of zeolites used as solid acids in petroleum refining include Pt/mordenite for C5/C6

5 isomerization, ZSM-5 for xylene isomerization and methanol-to-gasoline conversion, sulfided NiMo/faujasite for hydrocracking of heavy petroleum fractions, and USY for fluidized catalytic cracking. Zeolites are also used for other acid-catalyzed processes. The main difficulty in employing zeolites as acid catalysts lies in their great tendency to deactivate and their limited usefulness in reactions involving large molecules. Zeolites are

10 restricted to particular compositions, pore sizes and pore structures, which limit their applicability.

A plethora of non-zeolitic materials with surface acidic properties have been investigated as potential solid acid catalysts. Superacidity is beneficial for acid-catalyzed hydrocarbon reactions because lower operation temperatures are required. Moreover,

15 superacidic materials exhibit strong acidity and high activity for hydrocarbon reactions that are difficult to catalyze. Particularly interesting are the so-called "superacids", which have acidic strengths greater than 100% H₂SO₄. Sulfated zirconia and tungstated zirconia are well-studied examples of "superacidic" solids. Tungstated alumina is another example of a strongly acidic material.

20 The most challenging aspect in the isomerization of mid-distillates is to obtain high selectivity for isomerization vs. cracking at high conversion. Sulfated zirconia is active in converting hydrocarbons even at temperatures below 100°C, but it favors cracking reactions. Iglesia et al. (1996) found that at 200°C with about 50% n-heptane conversion, isomerization selectivities were 85% on Pt/WO₃/ZrO₂, but only 35% on Pt/SO₄²⁻/ZrO₂.

25 Currently, zeolites and tungstated zirconia are the two most studied solid acids for the isomerization of mid-distillates due to the selectivity and stability of these catalysts. The benefits of using non-zeolitic materials include greater compositional flexibility, and therefore greater control of surface acidity, higher thermal and hydrothermal stability, and lower catalyst cost.

30 Summary of the Invention

In certain embodiments, the catalytic compounds of the invention are represented by the generalized formula:



wherein:

R₁ is a metal or metal alloy or bimetallic system;

R₂ is any metal dopant;

R₃ is a metallic oxide or mixtures of any metallic oxide;

5 R₄ is selected from WO_x, MoO_x, SO₄²⁻ or PO₄³⁻; and

x is a whole or fractional number between 2 and 3 inclusive.

In a particular embodiment, R₁ is selected from a Group VIII noble metal or a combination of Group VIII noble metals. In another embodiment, R₁ is selected from platinum, palladium, iridium, rhodium, or a combination of these. In yet another 10 embodiment, R₁ is a Pt-Sn, Pt-Pd, or Pt-Ga alloy or bimetallic system.

In a particular embodiment, R₂ is selected from the group Al³⁺, Ga³⁺, Ce⁴⁺, Sb⁵⁺, Sc³⁺, Mg²⁺, Co²⁺, Fe³⁺, Cr³⁺, Y³⁺, Si⁴⁺, and In³⁺.

In another particular embodiment, R₃ is selected from the group zirconium oxide, titanium oxide, tin oxide, ferric oxide, cerium oxide or mixtures thereof. In another 15 particular embodiment, R₄ is selected from SO₄²⁻, WO_x, MoO_x, PO₄³⁻, W₂₀O₅₈, WO_{2.9} and anions and mixtures thereof. In a particular embodiment, the metallic oxide is ZrO₂. In a particular embodiment, x about 3.

In one embodiment, the ratio of metal dopant to metal in the oxide is less than or equal to about 0.20. In another embodiment, the ratio of metal dopant to metal in the oxide 20 is less than or equal to about 0.05. In yet another embodiment, the ratio of metal dopant to metal in the oxide is about 0.05.

In another embodiment, the catalytic compounds of the present invention are represented by Pt/WO₃/Al-ZrO₂.

Another aspect of this invention is a method of alkane and alkyl moiety 25 isomerizations comprising the step of contacting a catalyst with an alkane or alkyl, wherein said catalyst comprises:

R₁/R₄/R₂-R₃

wherein:

R₁ is a metal or metal alloy or bimetallic system;

30 R₂ is any metal dopant;

R₃ is a metallic oxide or mixtures of any metallic oxide;

R₄ is selected from WO_x, SO₄²⁻, MoO_x, or PO₄³⁻; and

x is a whole or fractional number between 2 and 3 inclusive.

In a preferred embodiment, the catalysts are used for conversion of straight chain or n-alkyls. In certain embodiments, the n-alkyl is a straight chain lower alkane, or C₄-C₇ alkane. In certain other embodiments, the n-alkyl is n-hexane, n-octane, or n-heptane. In a particular embodiment, the n-alkyl is n-heptane.

5 In one embodiment, the temperature of the reaction was lower than 210°C, lower than 170°C, lower than 150°C. In another embodiment, the isomerization conversions are higher than 80%. In yet another embodiment, the catalyst compounds are used in a process to produce alkane or alkyl moiety isomers with a yield of greater than 70%, greater than 80% of the reaction product. In a further embodiment, the catalyst compounds were used to 10 produce alkanes in the form of higher octane number, multi-branched alkanes.

Brief Description of the Figures

Figure 1 depicts the activity of Pt/WO₃/M-ZrO₂ with different dopants (M/Zr = 0.05, 800°C) in n-heptane isomerization.

15 Figure 2 depicts the effect of Al³⁺ doping level on the n-heptane isomerization activity of Pt/AlWZ(800°C).

Figure 3 depicts the n-heptane isomerization selectivity vs. conversion over Pt/AlWZ(0.05, 800°C) at 200°C in H₂.

Figure 4 depicts the n-heptane isomerization selectivity vs. conversion over Pt/AlWZ(0.05, 800°C) at 150°C in H₂.

20 Figure 5 depicts the octane number of n-heptane isomerization products and unconverted heptane over Pt/AlWZ(0.05, 800°C) in H₂.

Figure 6 depicts the n-hexane isomerization selectivity vs. conversion over Pt/AlWZ(0.05, 800°C) at 200°C in H₂.

25 Figure 7 depicts the octane number of n-hexane isomerization products and unconverted hexane over Pt/AlWZ(0.05, 800°C) at 200°C in H₂.

Figure 8 depicts the n-octane isomerization selectivity vs. conversion over Pt/AlWZ(0.05, 800°C) at 150°C in H₂.

Figure 9 depicts XRD patterns of WO₃/ZrO₂ with dopants (M/Zr = 0.05, 800°C).

30 Figure 10 depicts XRD patterns of Pt/WO₃/ZrO₂ with dopants (M/Zr = 0.05, 800°C) after reduction at 350°C in H₂.

Figure 11 depicts XRD patterns indicating ZrO₂ (111) peak shift in tungstated zirconia samples with different dopants (M/Zr = 0.05, 800°C).

Figure 12 depicts the change in ZrO_2 unit cell volume with the Al^{3+} doping level in Pt/AlWZ(800°C).

Figure 13 depicts the DRIFT spectra of pyridine adsorbed over 350°C-reduced (a) Pt/WZ(800°C), (b) Pt/AlWZ(0.05, 800°C) and (c) Pt/SiWZ(0.05, 800°C), obtained after 5 pyridine desorption at the specified temperatures.

Figure 14 depicts the temperature- programmed desorption of hydrogen over Pt/WZ(800°C), Pt/AlWZ(0.05, 800°C) and Pt/AlWZ(0.2, 800°C).

Figure 15 depicts the n-heptane conversion vs. reaction time over (a) Pt/AlWZ(0.05, 800°C) and (b) Pt/AlWZ(0.05, pH 10, 800°C) (reaction condition: 38 mg 10 catalyst, 200°C, ~6 % n-C₇ in H₂, VHSV = 110,000 hr⁻¹).

Figure 16 depicts the (i) n-heptane conversion and (ii) isomerization selectivity vs. reaction time over Pt/AlWZ(0.05, pH 10, 800°C) prepared with (a) $(\text{NH}_3)_4\text{Pt}(\text{NO}_3)_2$ and (b) H₂PtCl₆ (reaction condition: 38 mg catalyst, 200°C, ~6 % n-C₇ in H₂, VHSV = 110,000 hr⁻¹).

15 Figure 17a depicts n-heptane conversion vs. reaction time over AlWZ(0.05, 800°C) with (i) Pt, (ii) 4:1 Pt-Pd alloy, (iii) 1:5 Pt-Pd alloy and (iv) 1:5 Pt-Sn alloy (reaction condition: 38 mg catalyst, 200°C, ~6 % n-C₇ in H₂, VHSV = 110,000 hr⁻¹).

20 Figure 17b depicts isomerization selectivity vs. reaction time over AlWZ(0.05, 800°C) with (i) Pt, (ii) 4:1 Pt-Pd alloy and (iii) 1:5 Pt-Pd alloy (reaction condition: 38 mg catalyst, 200°C, ~6% n-C₇ in H₂, VHSV = 110,000 hr⁻¹).

Figure 18 depicts the effect of dopant oxides having similar crystal structure as ZrO_2 .

25 Figure 19a depicts n-butane conversion over reaction time and the effect of different anions on the activity of Pt/anion/Al-ZrO₂ (reaction condition: 250 mg catalyst, 250°C, ~2.47% n-C₄ in H₂, VHSV = 8,000 hr⁻¹).

Figure 19b depicts n-heptane conversion over reaction time and the effect of different anions on the activity and selectivity of Pt/anion/Al-ZrO₂ (reaction condition: 38 mg catalyst, 200°C, ~6% n-C₇ in H₂, VHSV = 110,000 hr⁻¹).

30 Detailed Description of the Invention

A. Overview

The present invention relates to a catalytic compound of anion-modified metal oxides doped with metal ions. The present invention also relates to n-alkane and alkyl moiety isomerization process comprising a catalytic compound of the present invention.

In certain embodiments, metallic dopants in a catalytic compound greatly increased 5 the activity of tungstated metal oxides with noble metals. These noble metal/anion/metal-doped metal oxide materials catalyzed the isomerization of n-alkanes and alkyl moieties with high selectivities.

In certain aspects of the present invention the catalytic materials are used in a 10 isomerization conversion reaction or process. Such a process has a low reaction temperature, and provides for high isomerization conversion yield.

B. Definitions

The term "alkyl" refers to the radical of saturated aliphatic groups, including straight-chain alkyl groups, branched-chain alkyl groups, cycloalkyl (alicyclic) groups, alkyl substituted cycloalkyl groups, and cycloalkyl substituted alkyl groups. In preferred 15 embodiments, a straight chain or branched chain alkyl has 30 or fewer carbon atoms in its backbone (e.g., C₁-C₃₀ for straight chain, C₃-C₃₀ for branched chain), and more preferably 20 of fewer. Likewise, preferred cycloalkyls have from 4-10 carbon atoms in their ring structure, and more preferably have 5, 6 or 7 carbons in the ring structure.

The terms "alkenyl" and "alkynyl" refer to unsaturated aliphatic groups analogous in 20 length and possible substitution to the alkyls described above, but which contain at least one double or triple carbon-carbon bond, respectively.

Unless the number of carbons is otherwise specified, "lower alkyl" as used herein 25 means an alkyl group, as defined above, but having from one to ten carbons, more preferably from one to six carbon atoms in its backbone structure. Likewise, "lower alkenyl" and "lower alkynyl" have similar chain lengths.

C. Compounds

The compounds of the invention are catalytic compounds represented by the 30 generalized formula:

R₁/R₄/R₂-R₃

wherein:

R₁ is a metal or metal alloy or bimetallic system;

R₂ is any metal dopant;

R_3 is a metallic oxide or mixtures of any metallic oxide;

R_4 is WO_x , MoO_x , SO_4^{2-} , or PO_4^{3-} ; and

x is a number between 2 and 3 inclusive.

In a particular embodiment, R_1 is selected from a Group VIII noble metal or a 5 combination of Group VIII noble metals. In another embodiment, R_1 is selected from platinum, palladium, iridium, rhodium, or a combination of these. In yet another embodiment, R_1 is a Pt-Sn, Pt-Pd, or Pt-Ge alloy or bimetallic system.

In a particular embodiment, R_2 is selected from the group Al^{3+} , Ga^{3+} , Ce^{4+} , Sb^{5+} , 10 Sc^{3+} , Mg^{2+} , Co^{2+} , Fe^{3+} , Cr^{3+} , Y^{3+} , Si^{4+} , and In^{3+} . In another embodiment, R_2 is Al^{3+} .

15 In another particular embodiment, the metallic oxide is zirconium oxide, titanium oxide, ferric oxide, cerium oxide, tin oxide, SO_4^{2-} , and anions and mixtures thereof. In a particular embodiment, the metallic oxide is ZrO_2 .

In another embodiment, x is about 3.

15 In one embodiment, the ratio of metal dopant to metal in the oxide is less than or equal to about 0.20. In another embodiment, the ratio of metal dopant to metal in the oxide is less than or equal to about 0.05. In yet another embodiment, the ratio of metal dopant to metal in the oxide is about 0.05.

In another embodiment, the catalytic compounds of the present invention are represented by $Pt/WO_3/Al-ZrO_2$.

20 In an aspect of the present invention, the catalytic compounds are used for conversion of straight chain alkyls to branched alkyls. In a preferred embodiment, the catalysts are used for conversion of straight chain or n-alkyls. As shown in Fig. 1, doping ZrO_2 with different cations changed the activity of $Pt/WO_3/ZrO_2$ dramatically. Dopants such as Al^{3+} and Ga^{3+} increased the catalyst activity by 2-3 times. This promotion effect is 25 not related to the acidity/basicity of the dopant oxide or to the reduction potential of the dopant cation. For example, MgO and Y_2O_3 are both basic oxides, but Mg^{2+} dopant increased the activity. The reduction potentials of Al^{3+} , Cr^{3+} , and Co^{2+} are very different from each other; however, they all increased the activity of tungstated zirconia with Pt.

30 Herein a shorthand notation for catalytic compounds is used. For example, $Pt/AlWZ(0.05, 800^\circ C)$ is a platinum tungstated zirconia catalyst doped with Al^{3+} with a ratio of Al/Zr of 0.05 and calcinated at $800^\circ C$.

In an embodiment, the ratio of Al to Zr is ≤ 0.05 . Different amounts of Al^{3+} ion were introduced into zirconia in the preparation of $\text{Pt/AlWZ}(800^\circ\text{C})$. Fig. 2 showed that at low doping levels ($\text{Al/Zr} \leq 0.05$), the activity of $\text{Pt/AlWZ}(800^\circ\text{C})$ increased with the amount of dopant. However, at high doping levels, the activity of $\text{Pt/AlWZ}(800^\circ\text{C})$ decreased with the amount of dopant. Doping Al^{3+} and Ga^{3+} ions into zirconia promoted the activity of $\text{Pt/WO}_3/\text{ZrO}_2$ by 2-3 times. Here, $\text{Pt/AlWZ}(0.05, 800^\circ\text{C})$ was chosen representatively to convert a series of mid-distillates, such as n-hexane, n-heptane and n-octane. The isomerization selectivities vs. total conversions of the three hydrocarbons are shown in Fig. 3 to Fig. 8.

10 In an embodiment, the catalyst is used in an isomerization reaction with a greater than 50% conversion, and a greater than 60% selectivity. At 200°C , 85% isomerization selectivity was obtained at 63% conversion of n-heptane over $\text{Pt/AlWZ}(0.05, 800^\circ\text{C})$ (Fig. 3). Considering that the conversion rate of n-heptane over $\text{Pt/AlWZ}(0.05, 800^\circ\text{C})$ was very high at 200°C (about $16 \mu\text{mol n-C}_7/\text{s/g}$ initially), the reaction temperature was lowered to 15 150°C . At 150°C , undoped $\text{Pt/WZ}(800^\circ\text{C})$ was not active, but $\text{Pt/AlWZ}(0.05, 800^\circ\text{C})$ was still active enough to convert n-C₇ at a rate of $1.1 \mu\text{mol/s/g}$ with a significantly improved isomerization selectivity. Isomerization selectivity was as high as 85% at 90% conversion of n-heptane (Fig. 4). Besides the overall isomerization selectivity, the percent of multi-branched isomers in the isomer products is of great interest since the octane numbers of 20 multi-branched isomers are much higher than that of mono-branched isomers. As shown in Fig. 4, the percent of multi-branched isomers increased rapidly with the percent conversion of n-heptane. Correspondingly, the octane number increased from 0 to 50 and 40 through n-heptane isomerization at 150°C and 200°C , respectively, over $\text{Pt/AlWZ}(0.05, 800^\circ\text{C})$ (Fig. 5).

25 In an embodiment, the catalyst of the present invention is used in an alkane or alkyl moiety isomerization reaction to increase the octane number. In another embodiment, $\text{Pt/AlWZ}(0.05, 800^\circ\text{C})$ increases the octane number to greater than 50, greater than 60. For example, the $\text{Pt/AlWZ}(0.05, 800^\circ\text{C})$ could convert n-hexane at a high rate of $3.2 \mu\text{mol/s/g}$ at 200°C . At 85% conversion, > 90% isomerization selectivity was maintained (Fig. 6). The 30 percent of multi-branched isomers in the isomerization products could reach 35% at 85% isomerization selectivity. As a result, the octane number increased from 32 to 66 through n-hexane isomerization at 200°C (Fig. 7).

The isomerization of n-octane over Pt/AlWZ(0.05, 800°C) may take place at 150°C with a rate of 6.4 $\mu\text{mol/s/g}$. The isomerization selectivity was also excellent (Fig. 8). At 80% conversion, 81% isomerization selectivity was obtained with 35% multi-branched isomers.

5 The chemical composition and physical properties of Pt/WO₃/ZrO₂ with different dopants are summarized in Table 1. Most dopants decreased the surface area of Pt/WO₃/ZrO₂, only Cr³⁺, In³⁺ and low Al³⁺ doping level led to a slight increase in surface area. When activity values were converted from the unit of $\mu\text{mol/s/g}$ to the unit of $\mu\text{mol/hr/m}^2$, the catalyst activity of Pt/MWZ(0.05, 800°C) still differed significantly 10 depending on the dopant introduced, and decreased in the order of Ga³⁺ \approx Al³⁺ > Mg²⁺ > Co²⁺ > Fe³⁺ > Cr³⁺ > Y³⁺ > Si⁴⁺ > In³⁺.

15 The X-ray diffraction (XRD) patterns of tungstated zirconia with dopants are shown in Fig. 9. No diffraction peaks of dopant oxides were noted, indicating that the dopants were highly dispersed. The ZrO₂ was present mainly in tetragonal phase with crystallite sizes of 13-18 nm. The WO₃ diffraction peak intensities were quite different in these samples. Stronger WO₃ peaks were found in the XRD patterns of tungstated zirconia doped with Al³⁺, Ga³⁺, Fe³⁺ and Y³⁺.

20 The Pt/MWZ catalysts were investigated by XRD after they were reduced at 350°C in H₂ (Fig. 10). It was shown that WO₃ was reduced to W₂₀O₅₈ after the pretreatment in H₂. Zirconia was not affected in the process except for minor increase in monoclinic phase in some doped samples.

25 Since there was no diffraction peak of dopant oxide in the XRD patterns of the various samples, the dopants must be highly dispersed. As most dopants are different in ionic radius from Zr⁴⁺, the substitution of Zr⁴⁺ by the dopant would lead to changes in the ZrO₂ unit cell. Using silicon as an internal reference in XRD studies, the position of 30 zirconia (111) peak for various doped samples were examined (Fig. 11). For dopants with a smaller ionic radius than Zr⁴⁺, the zirconia (111) peak did shift to higher angles except for SiWZ. Dopants with a larger ionic radius than Zr⁴⁺ caused the shift of zirconia (111) peak to lower angles. These findings suggested that all dopants except Si⁴⁺ could substitute for Zr⁴⁺ in the crystal structure of zirconia. For the Pt/SiWZ catalyst, Si was likely present as a silica gel coating instead of a structural dopant for ZrO₂; this silica gel might have

weakened the interaction between zirconia and tungsten oxide, resulting in the reduction in catalyst activity.

For Pt/AlWZ catalysts, the isomerization activity was maximized at a Al/Zr ratio of 0.05 (Fig. 2). Fig. 12 showed that the amount of zirconia unit cell volume reduction was 5 smaller when the Al/Zr ratio was increased beyond 0.05, which implied that some of the Al³⁺ dopants did not substitute for Zr⁴⁺ at high Al³⁺ loadings. Instead, they might have formed a surface Al₂O₃ coating, which compromised the promotional effect of Al³⁺ dopants in alkane isomerization.

The acidity of Pt/WO₃/ZrO₂ with and without dopants was characterized by 10 pyridine-adsorption with DRIFT spectroscopy. The catalyst was pretreated in air and then reduced in H₂ for 1.5 hr. The reduced sample was mixed with 20 wt% silica gel as an internal reference. After grinding to a fine powder with particle size below 74 μ m, the sample was loaded into the DRIFT cell. The sample was pretreated in dry He at 450°C for 1 hr before pyridine was introduced at room temperature. After 30 min of pyridine 15 adsorption, the sample was purged in flowing He at 150°C, 250°C and 350°C for 1 hr. DRIFT spectrum was taken near the end of purging at each desorption temperature. The DRIFT spectra of three representative samples, Pt/WZ(800°C), Pt/AlWZ(0.05, 800°C) and Pt/SiWZ(0.05, 800°C), are shown in Fig. 13. The peak intensities of adsorbed pyridine on each sample were normalized to the Si-O-Si peak intensity at 1862 cm⁻¹. The peaks at 1540 20 cm⁻¹ and 1445 cm⁻¹ correspond to Brønsted and Lewis acid sites, respectively. At each desorption temperature, the least active Pt/SiWZ(0.05, 800°C) had very weak peaks at 1540 cm⁻¹ and 1445 cm⁻¹ compared to Pt/WZ(800°C) and Pt/AlWZ(0.05, 800°C). The quantitative comparison of peak intensities at 1540 cm⁻¹ and 1445 cm⁻¹ for different doped samples are listed in Table 2. Most dopants, except Si⁴⁺ and Fe³⁺, did not change the acidity 25 of Pt/WO₃/ZrO₂ by very much. Si⁴⁺ dopant reduced the amount of the acid sites dramatically and there were negligible strong acid sites in Pt/SiWZ(0.05, 800°C). Fe³⁺ dopant led to fewer and weaker Brønsted acid sites. For Pt/AlWZ, a higher doping level of Al/Zr = 0.2 led to reduced Brønsted acidity. Strong acid sites were important and necessary for the isomerization reaction, but not the only factor in determining the activity of the 30 catalyst.

The amount of H₂ adsorbed over the catalysts was measured through temperature-programmed desorption of hydrogen (H₂-TPD) over doped and undoped catalysts. The

catalysts were pretreated under the same condition as that prior to the reaction. After the adsorption of H₂ at 30°C for 2 hr, the samples were exposed to flowing argon to remove weakly adsorbed hydrogen. Then H₂ desorption study was initiated by heating the catalyst bed at a rate of 5°C/min in flowing argon under atmospheric pressure, and the effluent gas 5 was analyzed using a thermal conductivity detector. As shown in Fig. 14, H₂ desorption occurred about 150°C lower on Pt/AlWZ compared to Pt/WZ, and the total amount of H₂ desorbed from Pt/AlWZ(0.05, 800°C) was about 1.7 times of that from Pt/WZ(800°C). This difference in H₂ desorption characteristics might account for the difference in catalyst 10 activity between doped and undoped Pt/WZ sample. The abnormally high H₂/Pt molar ratio suggested a H₂ spillover effect. Since Pt dispersion over these samples was similar and no difference in Pt binding energy was observed from X-ray photoelectron spectroscopy (SSX-100 ESCA Spectrometer), the lower H₂ desorption temperature and greater H₂ desorption amount over Pt/AlWZ(0.05, 800°C) could be attributed to structural changes from the inclusion of Al³⁺.

15 In one embodiment, the metallic dopant is introduced at controlled pH values. In another embodiment, the metallic dopant is introduced at pH 10. Because the initial precipitation pH values for Zr⁴⁺ and various dopants were different, the precipitation of Zr⁴⁺ and dopants may begin at different points in time. By controlling pH precipitation the catalyst nanostructure and composition may be optimized. To increase the homogeneity of 20 the doped zirconia, Zr⁴⁺ and dopant cations were precipitated under a constant pH of 10 (see Example 5). By using controlled pH precipitation, the catalyst obtained (Pt/AlWZ(0.05, pH 10, 800°C)) gave rise to significantly higher activity compared to Pt/AlWZ(0.05, 800°C) (see Fig. 15).

25 The precursor used for Pt also affected the activity and selectivity of the resulting Pt/AlWZ(0.05, pH 10, 800°C) (Fig. 16). By using (NH₃)₄Pt(NO₃)₂ as the Pt precursor instead of H₂PtCl₆, a more active and selective Pt/AlWZ(0.05, pH 10, 800°C) catalyst was obtained for the isomerization of n-heptane. In one embodiment, the noble metal may be varied to optimize isomerization of n-alkyls; however, it is also possible to use non-noble metals in the isomerization catalysts. Table 3 shows various noble metals in the compound 30 of the present invention. In another embodiment, a noble metal alloy may be used (Figure 17).

In an embodiment, the 1:5 Pt-Pd alloy could be used to give a slightly higher activity than Pt for AlWZ(0.05, 800°C), but the latter provided for a higher isomerization selectivity. Other alloys such as Pt-Sn or Pt-Ge may be used to reduce the initial catalyst deactivation while retaining the high isomerization selectivity of the AlWZ system.

5 In one embodiment, the dopant metals may be varied to optimize catalytic behavior. Figure 18 shows the isomerization of n-alkanes using various dopant oxides with 38 mg of catalyst reduced at 350°C in H₂ for 1.5 hours. The reaction was run at 200°C. In an embodiment, the metallic oxide anion may be varied to optimize isomerization selectivity. In another embodiment, the metallic oxide anion is SO₄²⁻ or WO₃ (Figure 19).

10 Nanocomposite Pt/tungstated zirconia catalysts with dopants such as Al³⁺ and Ga³⁺ were much more active and selective than conventional Pt/tungstated zirconia in the isomerization of hexane, heptane and octane. Nanocomposite processing provides for an ultrahigh dispersion of components, allowing for the effective substitution of dopant cations within the zirconia lattice. The resulting Pt/tungstated doped zirconia allows for low-
15 temperature conversion of mid-distillates, greater H₂ adsorption, and a low H₂ desorption temperature. Such system may also be used for the effective isomerization of other hydrocarbons with negligible catalyst deactivation over time.

Table 1. Chemical Composition and Physical Properties of Various Doped Pt/WO₃/ZrO₂.

Sample	Chemical Composition*			S. A. (m ² /g)	Activity at 2 hr TOS	
	Dopant/Zr	W (wt%)	Pt (wt%)		(μmol/s/g)	(μmol/hr/m ²)
Pt/WZ(800°C)	0	16	1.0	63	5.0	286
Pt/AlWZ(0.05, 800°C)	0.05	16	1.0	56	12.9	829
Pt/GaWZ(0.05, 800°C)	0.05	16	1.0	57	13.2	834
Pt/CoWZ(0.05, 800°C)	0.05	16	1.0	60	8.9	534
Pt/MgWZ(0.05, 800°C)	0.05	16	1.0	53	9.0	611
Pt/FeWZ(0.05, 800°C)	0.05	16	1.0	49	5.4	397
Pt/CrWZ(0.05, 800°C)	0.05	16	1.0	77	7.5	351
Pt/YWZ(0.05, 800°C)	0.05	16	1.0	48	3.5	263
Pt/InWZ(0.05, 800°C)	0.05	16	1.0	68	0.17	9
Pt/SiWZ(0.05, 800°C)	0.05	16	1.0	22	0.12	20
Pt/AlWZ(0.025, 800°C)	0.025	16	1.0	65	9.9	548
Pt/AlWZ(0.1, 800°C)	0.1	16	1.0	44	9.2	753
Pt/AlWZ(0.2, 800°C)	0.2	16	1.0	37	4.3	418

* Nominal composition from synthesis conditions.

Table 2. The Amount of Brønsted and Lewis Acid Sites in Reduced Pt/WO₃/ZrO₂ With and Without Dopants.

Sample	Desorption Temperature (°C)	Brønsted Acid Sites*	Lewis Acid Sites*
Pt/WZ(800°C)	150	0.46	0.93
	250	0.28	0.43
	350	0.14	0.25
Pt/AlWZ(0.05, 800°C)	150	0.54	0.51
	250	0.26	0.46
	350	0.12	0.32
Pt/SiWZ(0.05, 800°C)	150	0.096	0.098
	250	0.050	0.031
	350	0.029	0.023
Pt/GaWZ(0.05, 800°C)	250	0.29	0.33
	350	0.18	0.25
Pt/CoWZ(0.05, 800°C)	250	0.35	0.50
	350	0.17	0.35
Pt/MgWZ(0.05, 800°C)	250	0.36	0.46
	350	0.18	0.34
Pt/CrWZ(0.05, 800°C)	250	0.34	0.90
	350	0.15	0.63
Pt/FeWZ(0.05, 800°C)	250	0.17	0.31
	350	0.067	0.27
Pt/YWZ(0.05, 800°C)	250	0.25	0.42
	350	0.11	0.21
Pt/InWZ(0.05, 800°C)	250	0.35	0.51
	350	0.15	0.33
Pt/AlWZ(0.2, 800°C)	150	0.28	0.72
	250	0.16	0.50
	350	0.077	0.32

* The amounts of Brønsted and Lewis acid sites were determined by the ratio of peak intensity at 1540 cm⁻¹ and 1445 cm⁻¹, respectively, over the peak intensity at 1862 cm⁻¹.

Table 3. Influence of Different Noble Metals.

Metal	Loading (wt%)	Activity (μ mol/s/g)	Conversion (%)	Isomerization (%)	Multi-branched Isomers (%)
Ru	1.0	0.51	4.9	87.4	34.6
Pd	1.0	1.1	8.3	99.8	15.8
Pt	1.0	1.1	10.9	99.8	15.3
	0.1	0.15	5.8	91.4	34.5
	10.0	0.14	5.6	96.3	16.3

Exemplification

5 The invention now being generally described, it will be more readily understood by reference to the following examples, which are included merely for purposes of illustration of certain aspects and embodiments of the present invention, and are not intended to limit the invention.

Example 1

10 0.161 mol of $ZrOCl_2 \cdot 8H_2O$ (Aldrich) was mixed with 0.082 mol of $AlCl_3 \cdot 6H_2O$ (Aldrich) in a 600 ml glass beaker. 320 ml of H_2O were added to dissolve the salts with stirring. Then 14-28 wt% NH_4OH was added dropwise to the solution under vigorous stirring until the final pH of the precipitation mixture reached 9.0. After stirring for more than 1 hr, the precipitate was washed by distilled water and recovered through 15 centrifugation. Materials were usually washed 5-6 times to remove the chloride ions.

The precipitate was dried in oven at 120°C overnight. Then, a calculated amount of ammonium metatungstate (99.9%, Strem) was added to the mixed hydroxide via the incipient wetness technique. After calcination at 600-950°C for 3 hr, the tungstated Al^{3+} -doped zirconia obtained was impregnated with 1 wt% of Pt using the precursor 20 $(NH_3)_4Pt(NO_3)_2$. After calcination at 450°C for 3 hr, the final product was denoted as $Pt/AlWZ(x, y)$ (x = nominal atomic ratio of Al/Zr , y = calcination temperature for tungstated Al-doped zirconia). Pt-loaded tungstated zirconia materials not doped with Al^{3+} were denoted as $Pt/WZ(y)$.

Example 2

Different metal ions besides Al^{3+} were co-precipitated with Zr^{4+} at a dopant/Zr atomic ratio of 0.05, following the procedures described in Example 1. The chloride or nitrate salts of metal ions, such as Ga^{3+} , Mg^{2+} , Co^{2+} , Cr^{3+} , Fe^{3+} , Y^{3+} , and In^{3+} , were mixed with zirconyl chloride. The final pH of the precipitation mixture for all materials was 9.0, 5 except for the Mg^{2+} -doped material, which was 10.0 to ensure complete Mg^{2+} precipitation. The final materials loaded with tungstate and Pt were denoted $\text{Pt}/\text{MWZ}(0.05, y)$, where M = dopant ion, y = calcination temperature for tungstate metal-doped zirconia.

Example 3

10 $\text{Si}(\text{IV})$ was co-precipitated with zirconyl chloride using an alkoxide precursor, $\text{Si}(\text{OC}_2\text{H}_5)_4$, at the final pH of 9.0. The final Si^{4+} -doped catalyst loaded with tungstate and Pt was denoted as $\text{Pt}/\text{SiWZ}(x, y)$.

Example 4

Example 1 was repeated with different amounts of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. Al/Zr ratios in the range of 0.025 to 0.20 were obtained.

15 Example 5

The same protocol as Example 1 was used, but the precipitation of Zr^{4+} and Al^{3+} was conducted under the controlled pH condition. The pH was maintained at 10 ± 0.2 by controlling the relative addition rate of the mixed salt solution to the addition rate of NH_4OH . The rest of the procedures was the same as that in Example 1. The final product 20 was denoted as $\text{Pt}/\text{AlWZ}(x, \text{pH } 10, y)$.

Example 6

Besides $(\text{NH}_3)_4\text{Pt}(\text{NO}_3)_2$, other Pt precursor such as H_2PtCl_6 was used in the loading of 1 wt% Pt over tungstated doped zirconia. In addition to pure Pt, Pt alloys and other noble metals were also loaded over the tungstated doped zirconia.

25 Example 7

Structural characterization

The microstructure and surface properties of the nanostructured solid acid materials were analyzed using a variety of experimental techniques. Powder X-ray diffraction (XRD) data were recorded on a Siemens D5000 diffractometer operated at 45 kV and 40 mA, using 30 nickel-filtered $\text{CuK}\alpha$ radiation with a wavelength of 1.5406 Å. Crystallite size was obtained by peak-broadening analysis using Scherrer's method. Nitrogen adsorption isotherms were obtained at 77 K on a Micromeritics ASAP 2010 Gas Sorption and

Porosimetry System. Samples were degassed at 150°C under vacuum until a final pressure of 1×10^{-3} Torr was reached. BET (Brunauer-Emmett-Teller) surface areas were determined over a relative pressure range of 0.05 to 0.20.

Example 8

5 *Catalyst acidity*

The acidity of tungstated doped zirconia catalyst was analyzed by pyridine-adsorption infrared (IR) spectroscopy. The sample was reduced at 350°C in H₂ for 1.5 hr before loading into a diffuse reflectance infrared Fourier-transform (DRIFT) cell. Amorphous silica was physically mixed with the sample as an internal standard (20 wt% 10 SiO₂ total). The sample was pretreated in He at 450°C for 1 hr before adsorption of pyridine at room temperature. IR spectra of the sample were recorded after desorption of pyridine in flowing He (45 ml/min) for 1 hr at 150°C, 250°C and 350°C on a Bio-Rad FTS-60A infrared spectrometer. The peak area of Si-O-Si at 1862 cm⁻¹ was used as the reference. The amounts of Brønsted acid and Lewis acid in the sample were linearly related 15 to the peak areas at 1540 cm⁻¹ and 1445 cm⁻¹ respectively, so these peak areas could be used in the comparison of the amount of acidic sites in different samples.

Example 9

Catalytic activity

The isomerization of n-heptane was carried out in a downflow fixed-bed reactor 20 under ambient pressure. The reaction took place at 150°C or 200°C. The catalyst was secured in place with pretreated quartz wool just above a thermocouple. n-Heptane was brought into the reactor by H₂ flowing through n-heptane saturator at 25°C, with a H₂/n-heptane molar flow ratio of 16. The flow rate of H₂ or the amount of catalyst loaded was adjusted to get the desired conversion of n-heptane. For comparing different catalyst 25 activity, n-heptane conversion was limited to about 20% to eliminate the effect of intraparticle mass transfer. The catalyst was pretreated in flowing air at 450°C for 1.5 hr before contacting with the feed gas. The reaction products were analyzed by a HP 6890 gas chromatograph equipped with a flame ionization detector (FID) and with a 50-m HP-PLOT/Al₂O₃ "KCl" deactivated capillary column. Isomerization reactions of n-hexane and 30 n-octane were performed under the same conditions as above except under different partial pressures. The n-hexane saturator was immersed in an ice trap to obtain a H₂/n-hexane

molar flow ratio of 16, and the n-octane saturator was set at 25°C to obtain a H₂/n-octane molar flow ratio of 53.

Incorporation by Reference

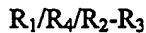
All publications and patents mentioned herein are hereby incorporated by reference 5 in their entirety, as if each individual publication or patent was specifically and individually indicated to be incorporated by reference. In case of conflict, the present application, including any definitions herein, will control.

Equivalents

Those skilled in the art will recognize, or be able to ascertain using no more than 10 routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the following claims.

We claim:

1. A catalytic compound represented by the generalized formula:



wherein:

- 5 R_1 is a metal or metal alloy or bimetallic system;
- R_2 is any metal dopant;
- R_3 is a metallic oxide or mixtures of any metallic oxide;
- R_4 is selected from WO_x , MoO_x , SO_4^{2-} or PO_4^{3-} ; and
- x is a whole or fractional number between 2 and 3 inclusive.
- 10 2. The catalytic compound of claim 1, wherein R_1 is a Group VIII metal.
3. The catalytic compound of claim 1, wherein R_1 is a combination of Group VIII metals.
4. The catalytic compound of claim 2, wherein R_1 is selected from platinum, palladium, iridium, rhodium, or a combination of these.
- 15 5. The catalytic compound of claim 1, wherein R_1 is selected from an alloy or bimetallic systems Pt-Sn, Pt-Pd, or Pt-Ge.
6. The catalytic compound of claim 1, wherein R_2 is selected from the group Al^{3+} , Ga^{3+} , Ce^{4+} , Sb^{5+} , Sc^{3+} , Mg^{2+} , Co^{2+} , Fe^{3+} , Cr^{3+} , Y^{3+} , Si^{4+} , and In^{3+} .
7. The catalytic compound of claim 6, wherein R_2 is Al^{3+} .
- 20 8. The catalytic compound of claim 1, wherein R_3 is selected from zirconium oxide, titanium oxide, tin oxide, ferric oxide, or cerium oxide.
9. The catalytic compound of claim 8, wherein R_3 is ZrO_2 .
10. The catalytic compound of claim 1, wherein the ratio of metal dopant to metal in the oxide is less than or equal to about 0.20.
- 25 11. The catalytic compound of claim 10, wherein the ratio of metal dopant to metal in the oxide is less than or equal to about 0.05.
12. The catalytic compound of claim 10, wherein the ratio of metal dopant to metal in the oxide is about 0.05.
13. The catalytic compound of claim 1, wherein R_4 is WO_x , wherein x is a whole or fractional number between 2 and 3 inclusive.
- 30 14. The catalytic compound of claim 13, wherein x is about 3.
15. The catalytic compound of claim 13, wherein x is about 2.9.

16. A method of alkane or alkyl moiety isomerization comprising the reaction step of contacting a catalyst with an alkyl, wherein said catalyst is selected from the compounds represented by the generalized structure:

5 $R_1/R_4/R_2-R_3$

wherein:

R_1 is a metal or metal alloy or bimetallic system;

R_2 is any metal dopant;

R_3 is a metallic oxide or mixtures of any metallic oxide;

10 R_4 is selected from WO_x , MoO_x , SO_4^{2-} or PO_4^{3-} ; and

x is a whole or fractional number between 2 and 3 inclusive.

17. The method of claim 16, wherein the alkane isomerization is a straight chain alkane isomerization.

18. The method of claim 17, wherein the alkane isomerization is a C_4-C_{10} alkane isomerization.

15 19. The method of claim 18, wherein the alkyl isomerization is C_6-C_8 alkane isomerization.

20 20. The method of claim 16, wherein the reaction step occurs at less than 210 °C.

20 21. The method of claim 16, wherein the reaction step occurs at less than 170 °C.

22. The method of claim 16, wherein the reaction step occurs at less than 150 °C.

23. The method of claim 16, wherein the reaction yield is greater than 70%.

25 24. The method of claim 23, wherein the reaction yield is greater than 80%.

25. The method of claim 16, wherein the alkane isomerization increases the octane number of the alkane.

26. The catalytic compound represented by the formula $Pt/WO_3/Al-ZrO_2$.

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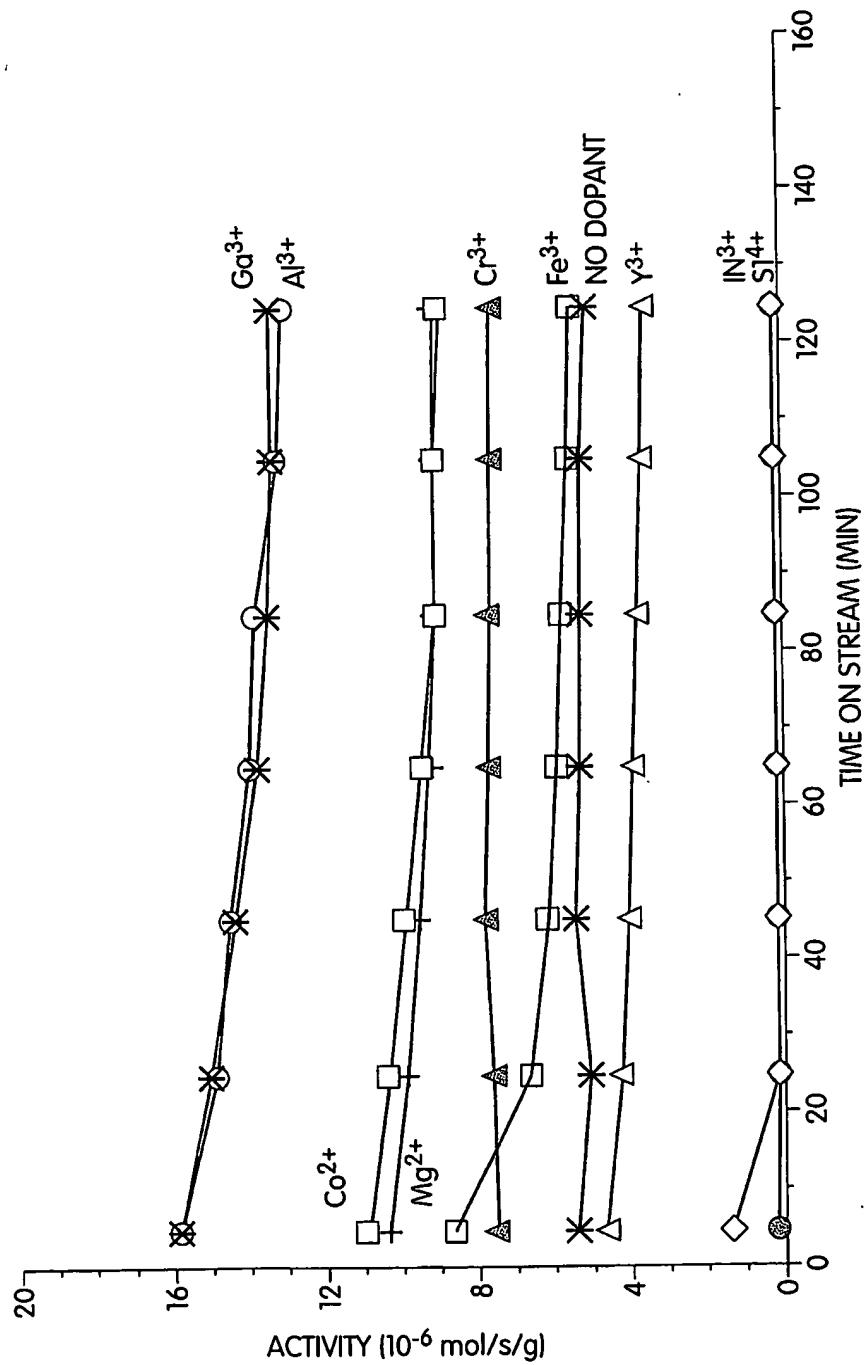


Fig. 1

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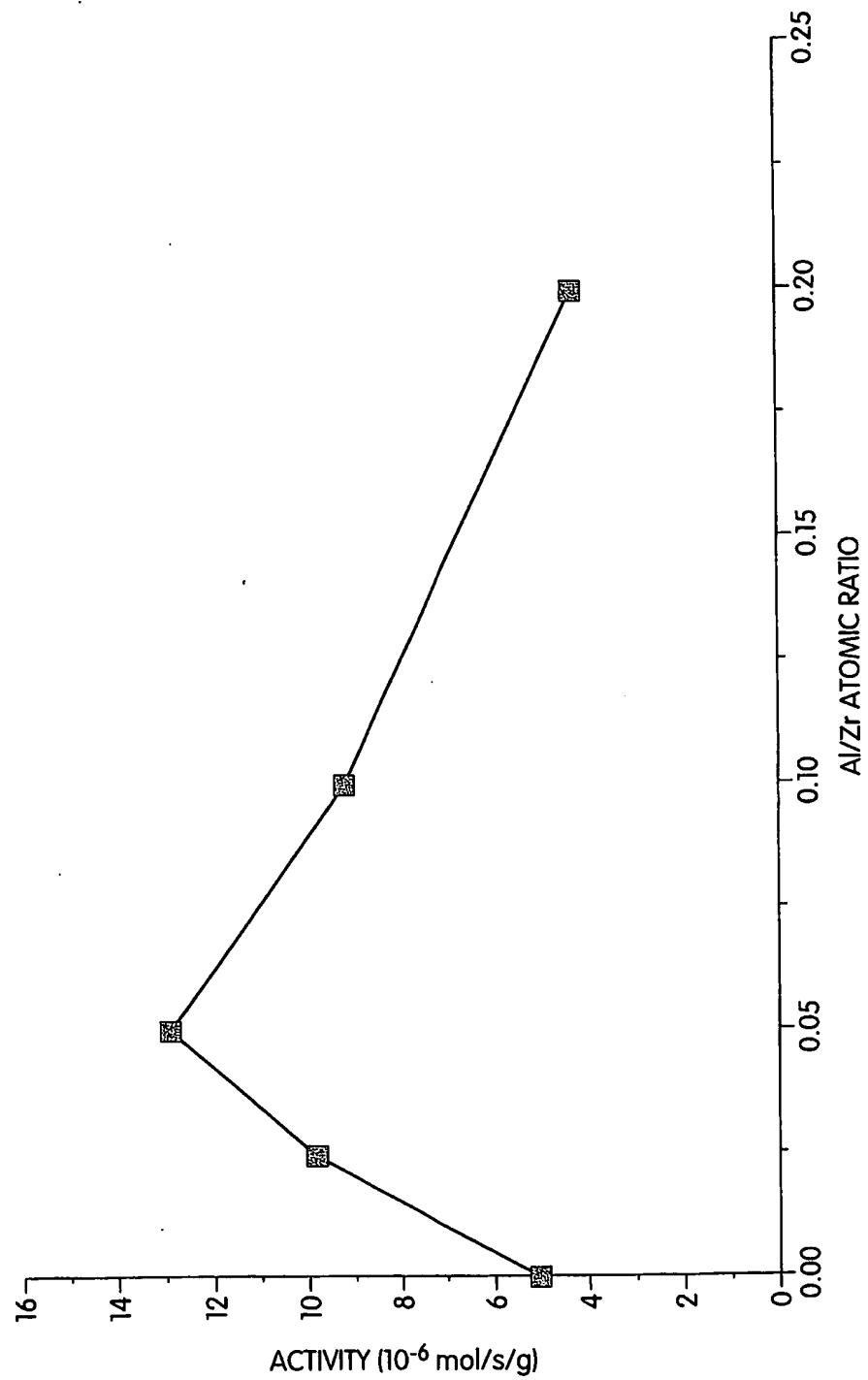


Fig. 2

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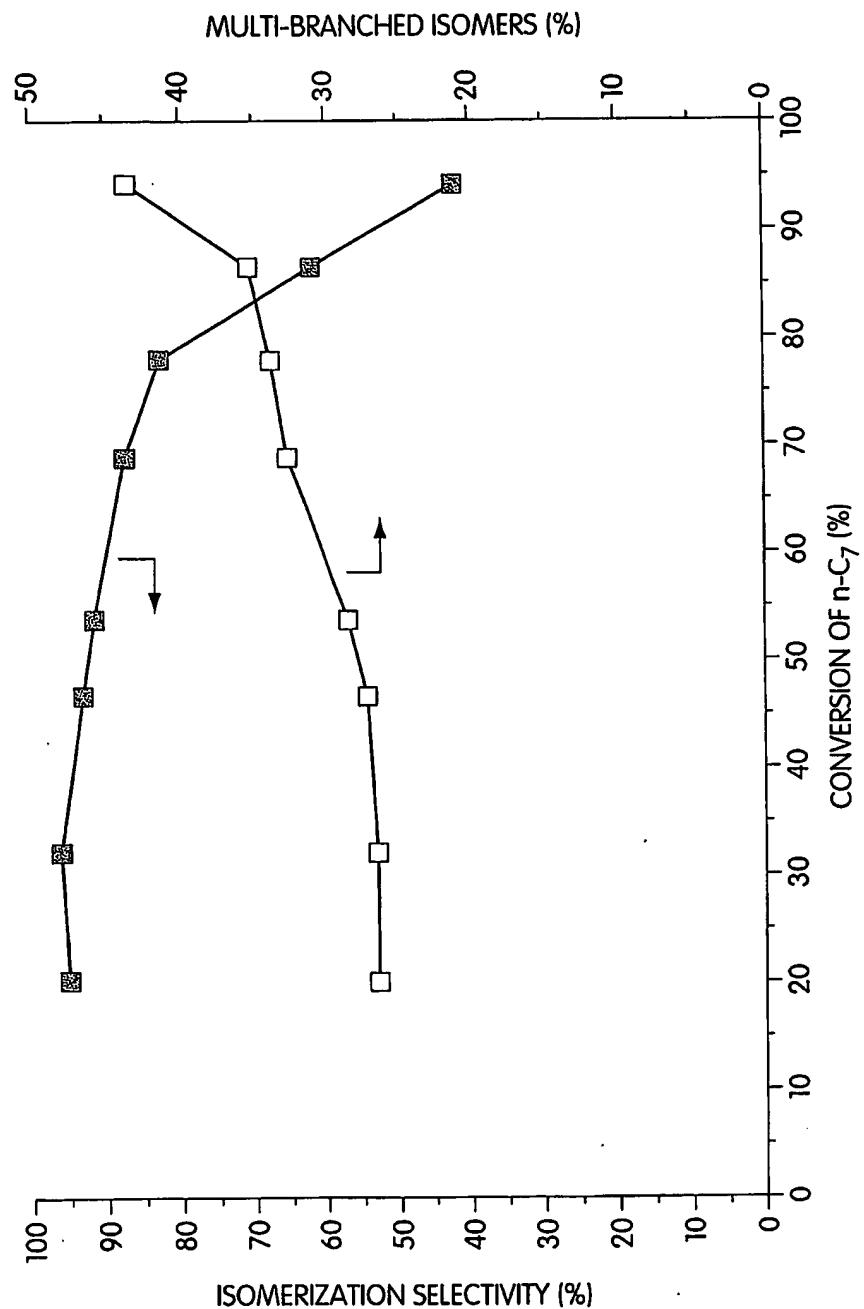


Fig. 3

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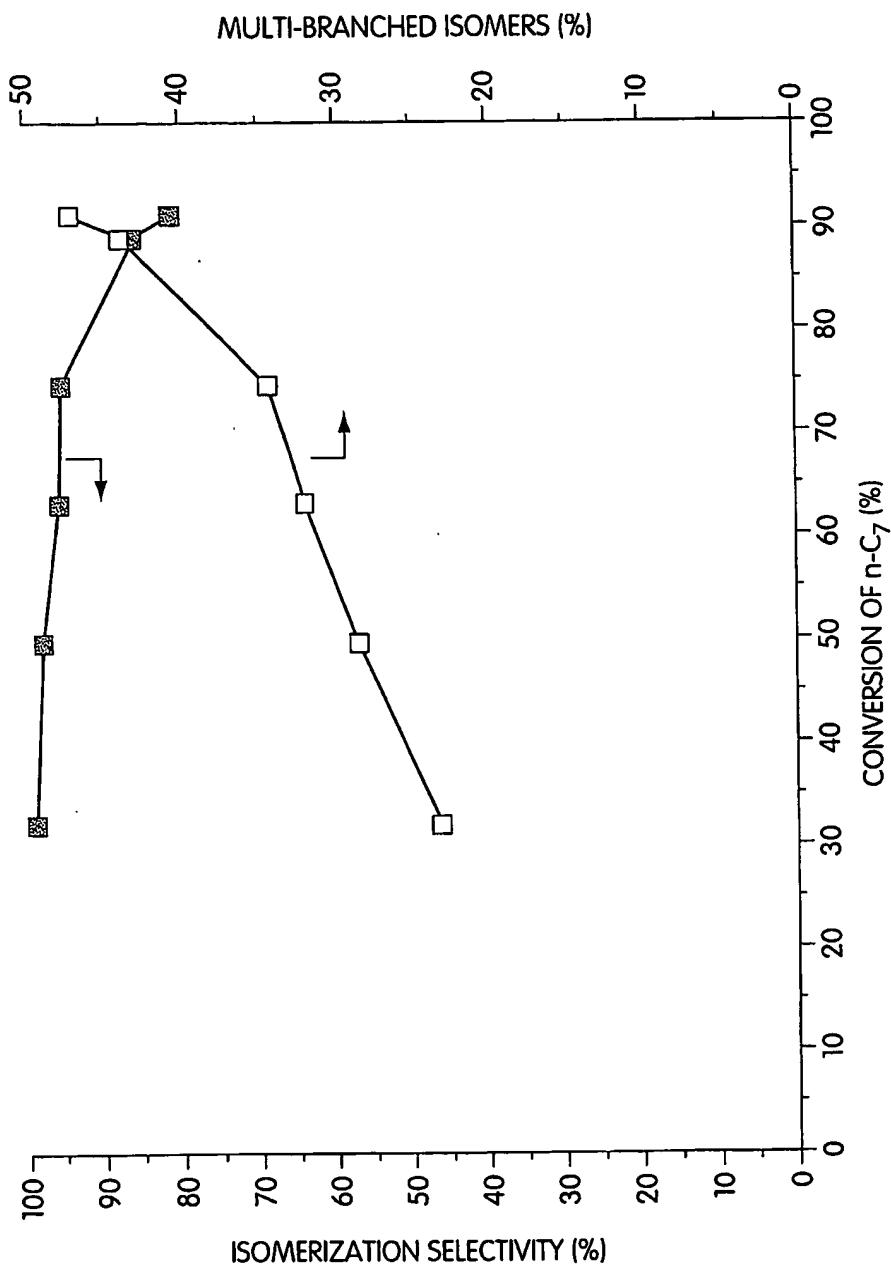


Fig. 4

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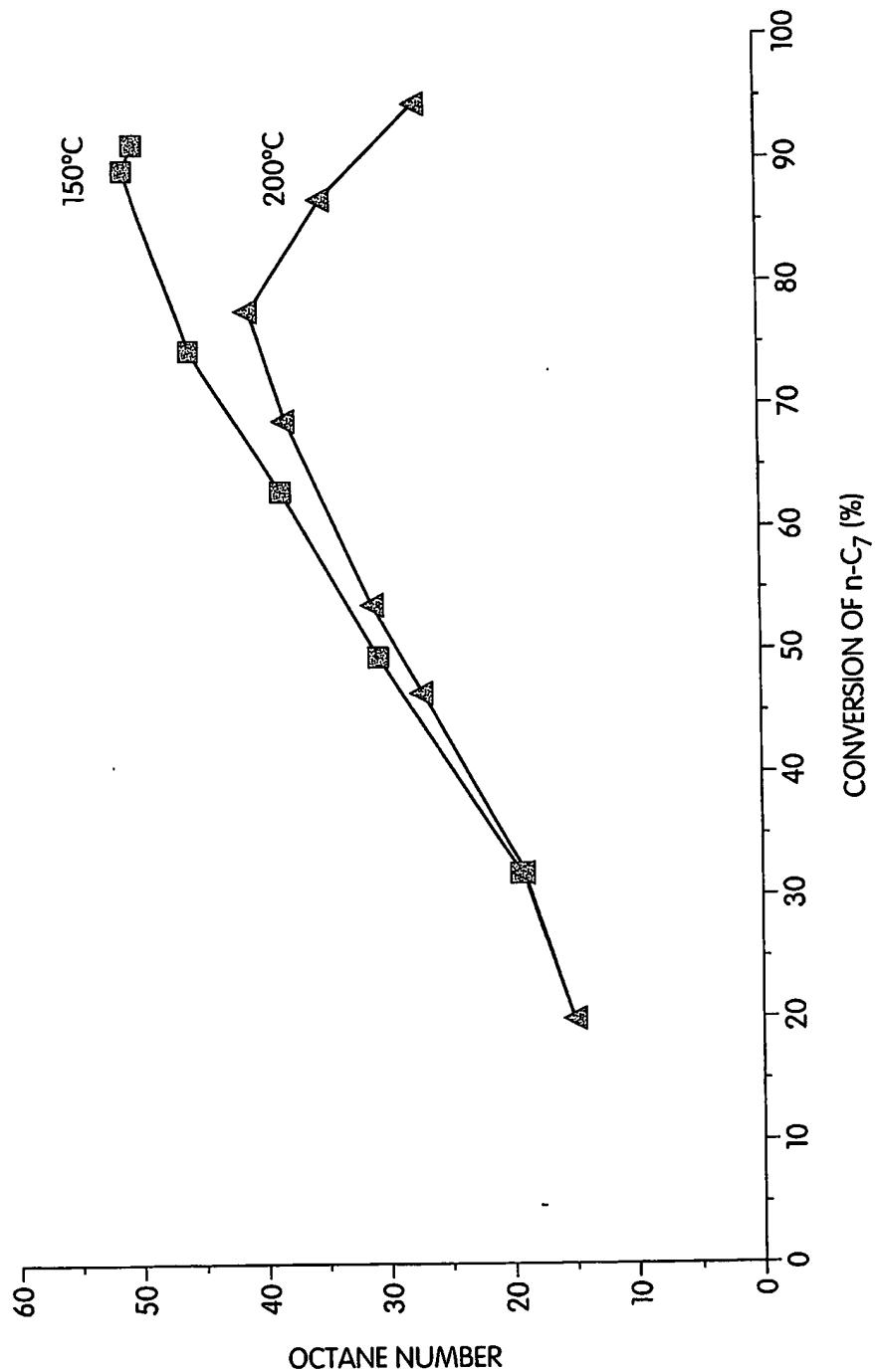


Fig. 5

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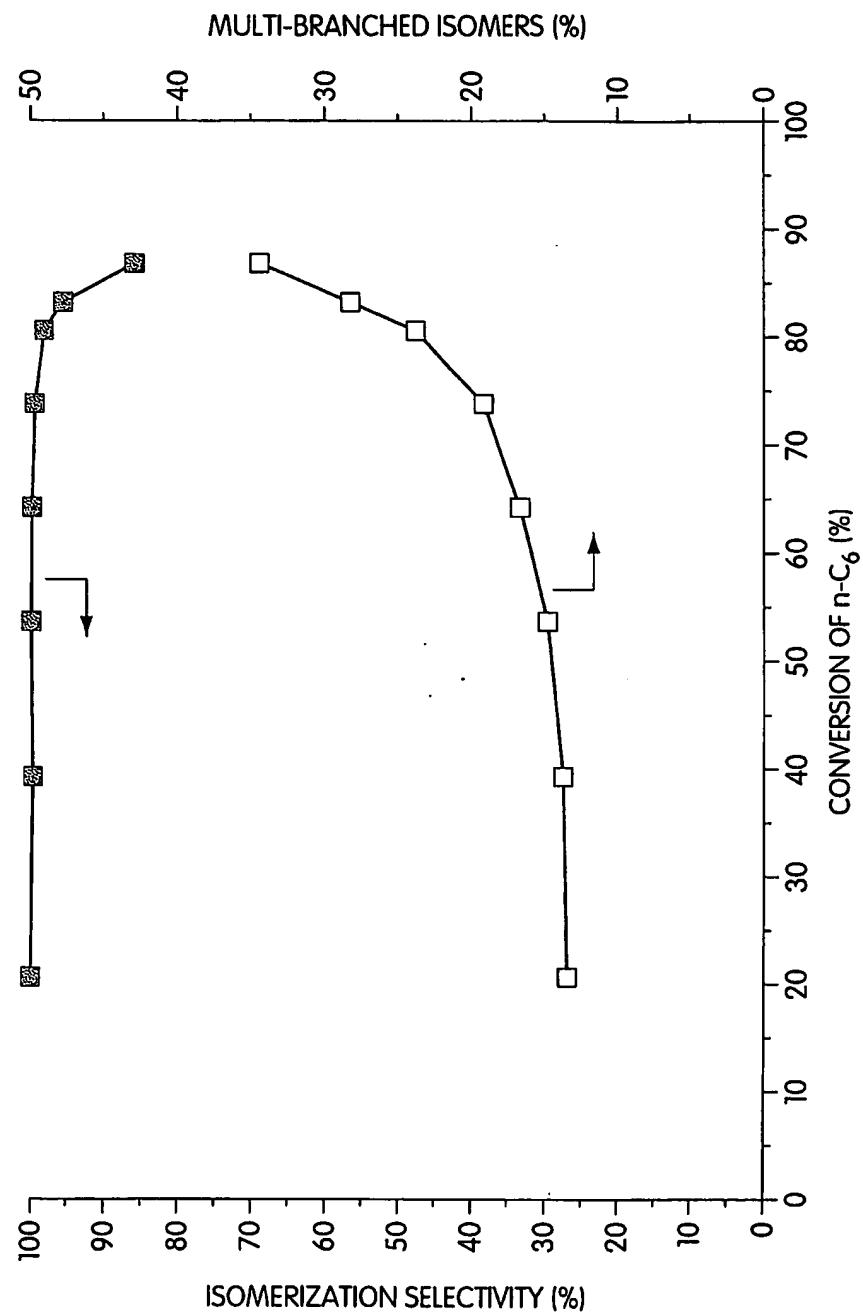


Fig. 6

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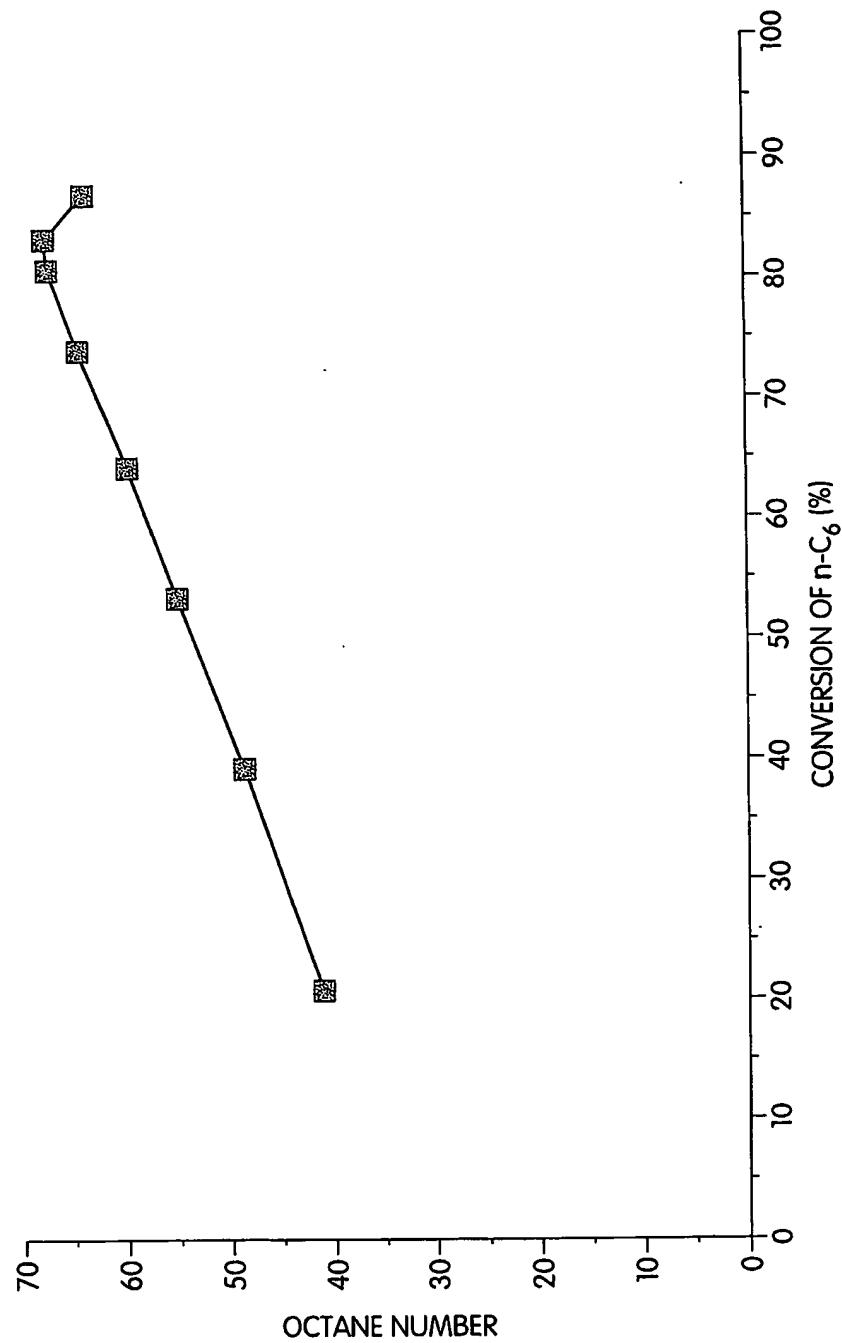


Fig. 7

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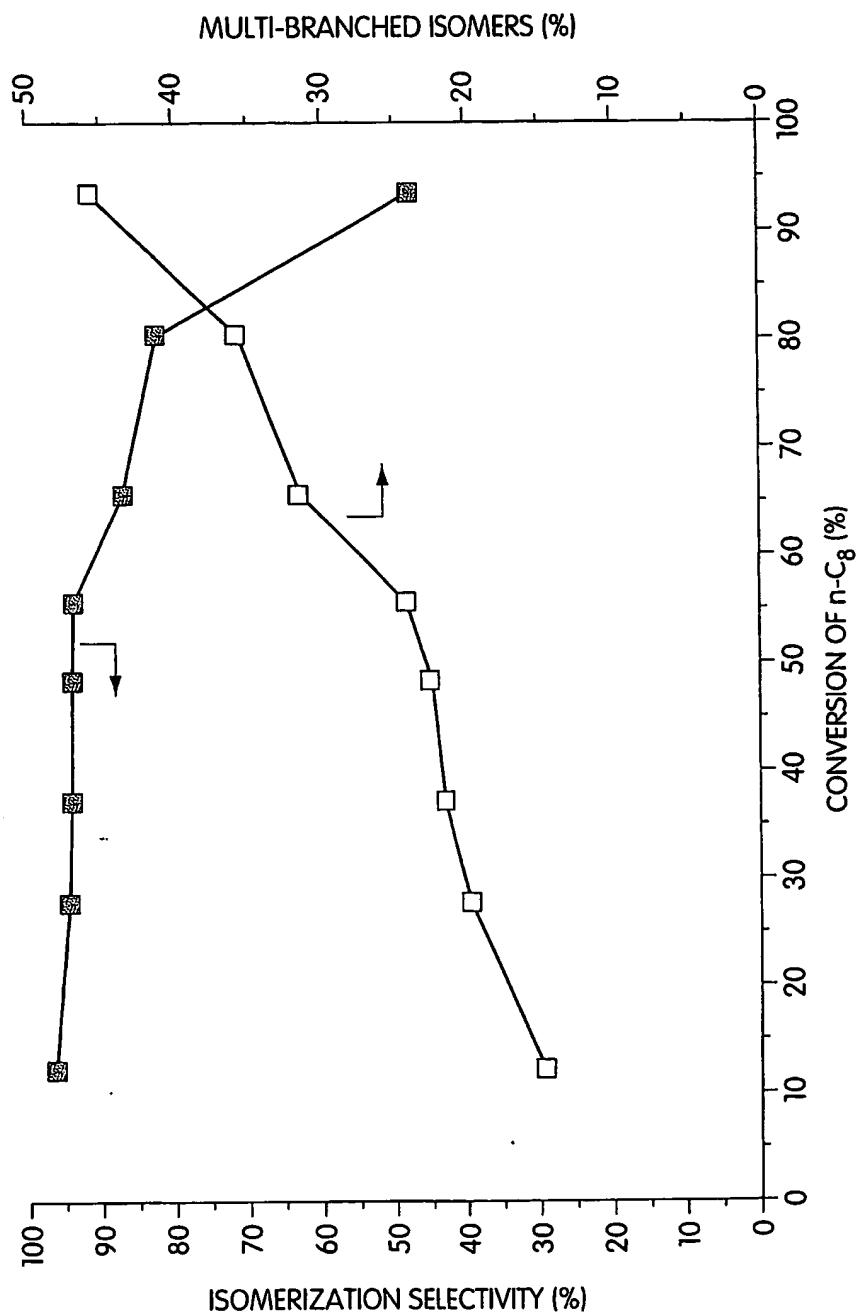


Fig. 8

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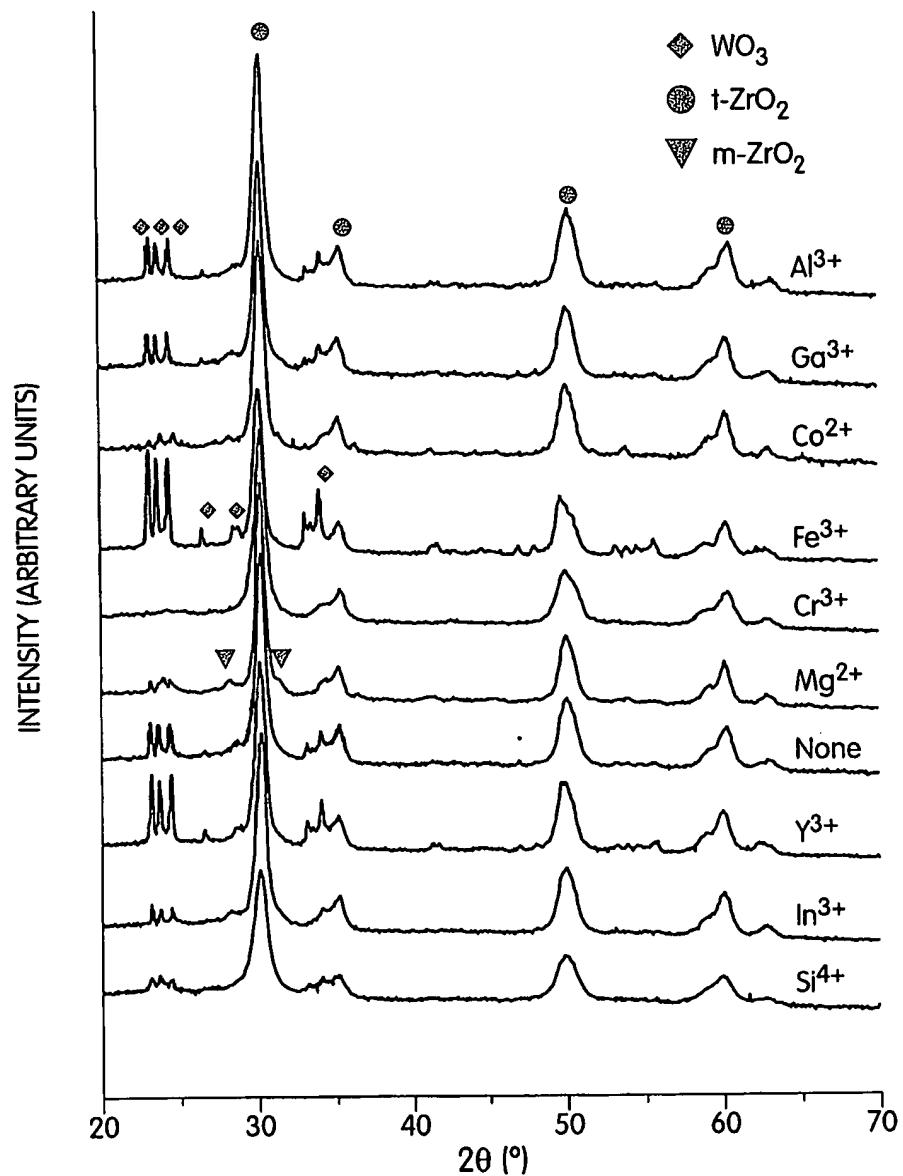


Fig. 9

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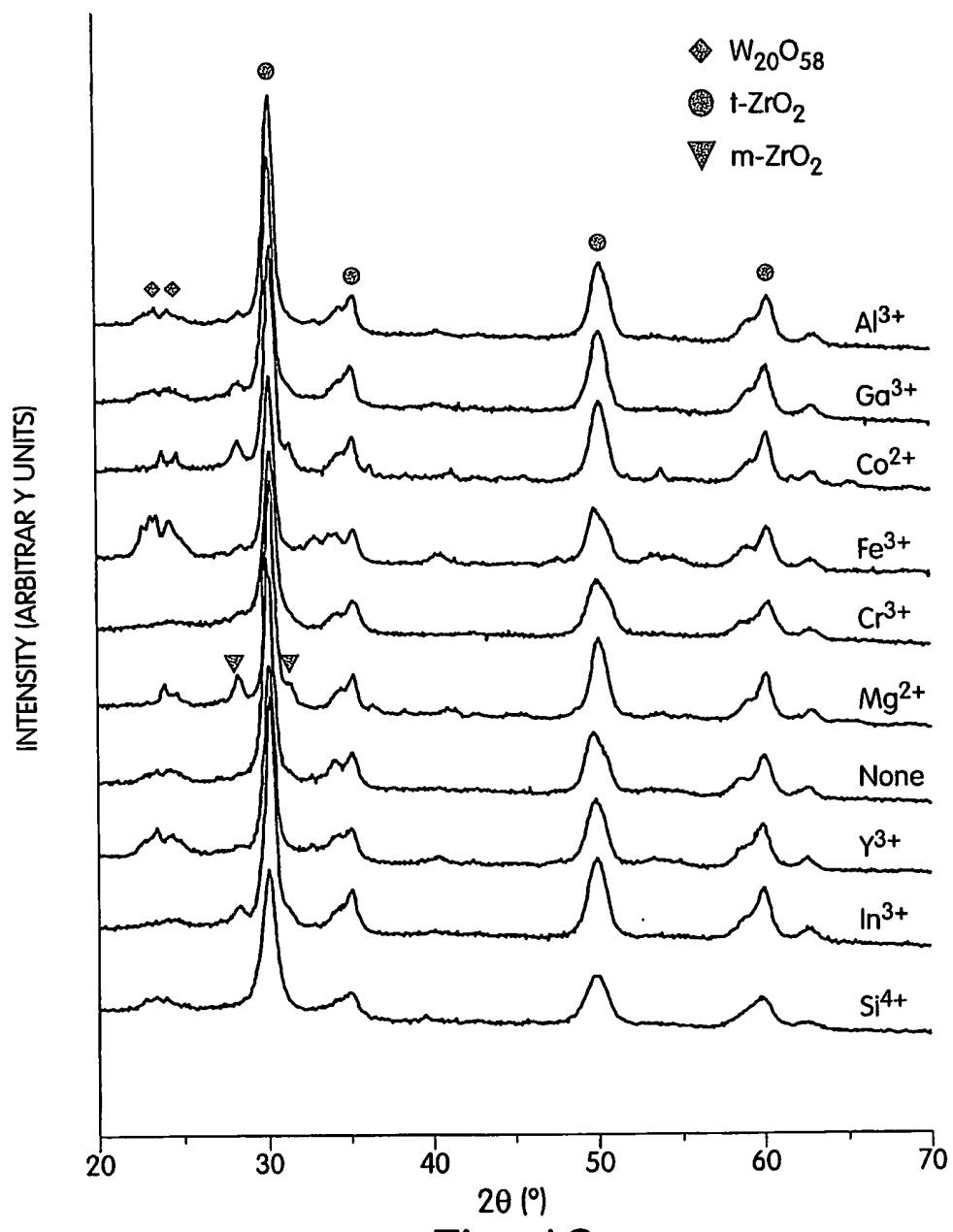


Fig. 10

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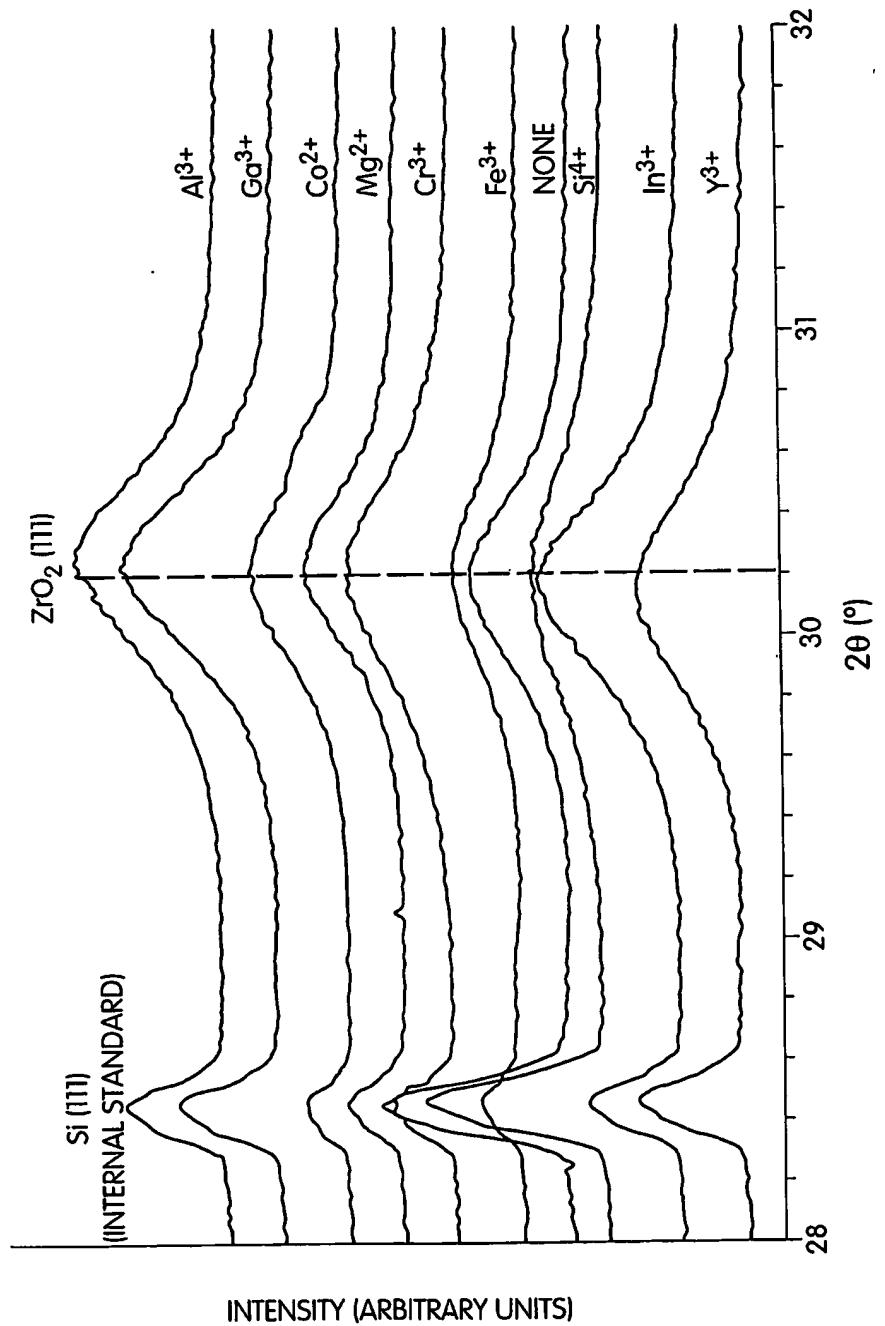


Fig. 11

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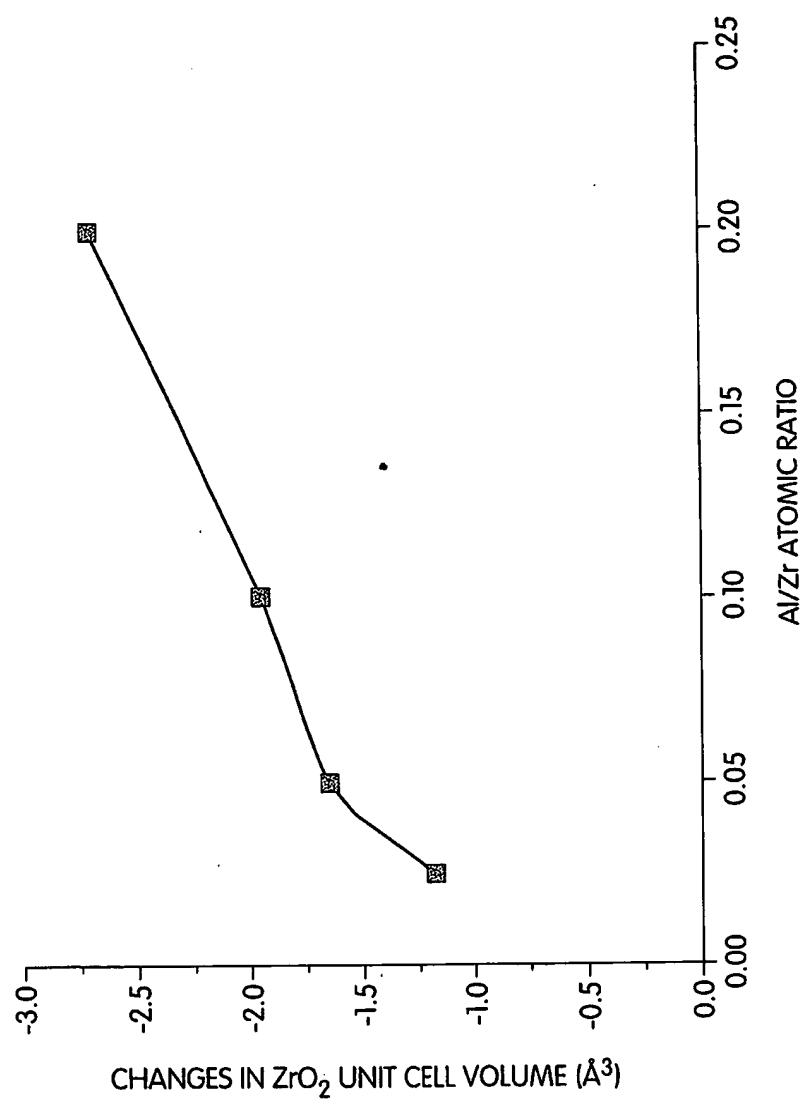


Fig. 12

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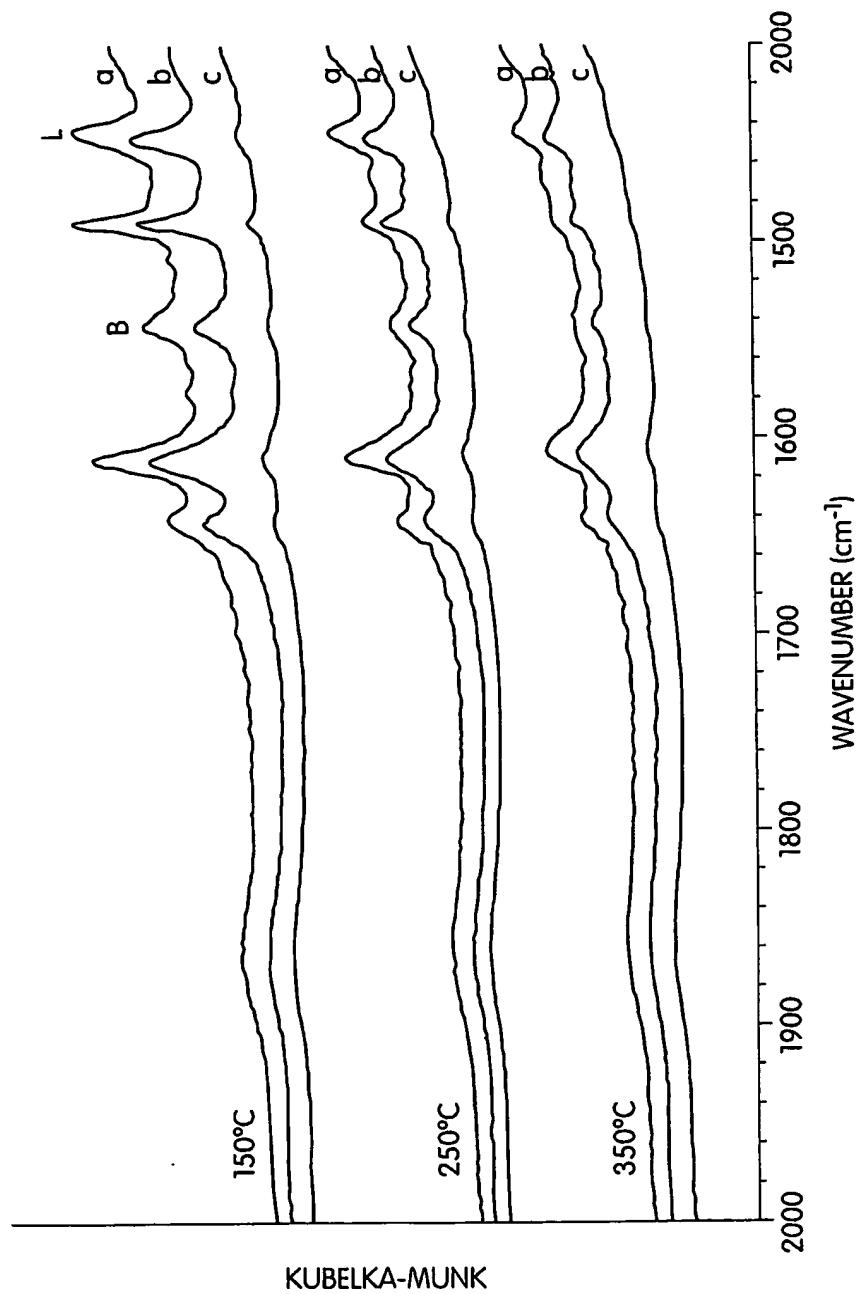
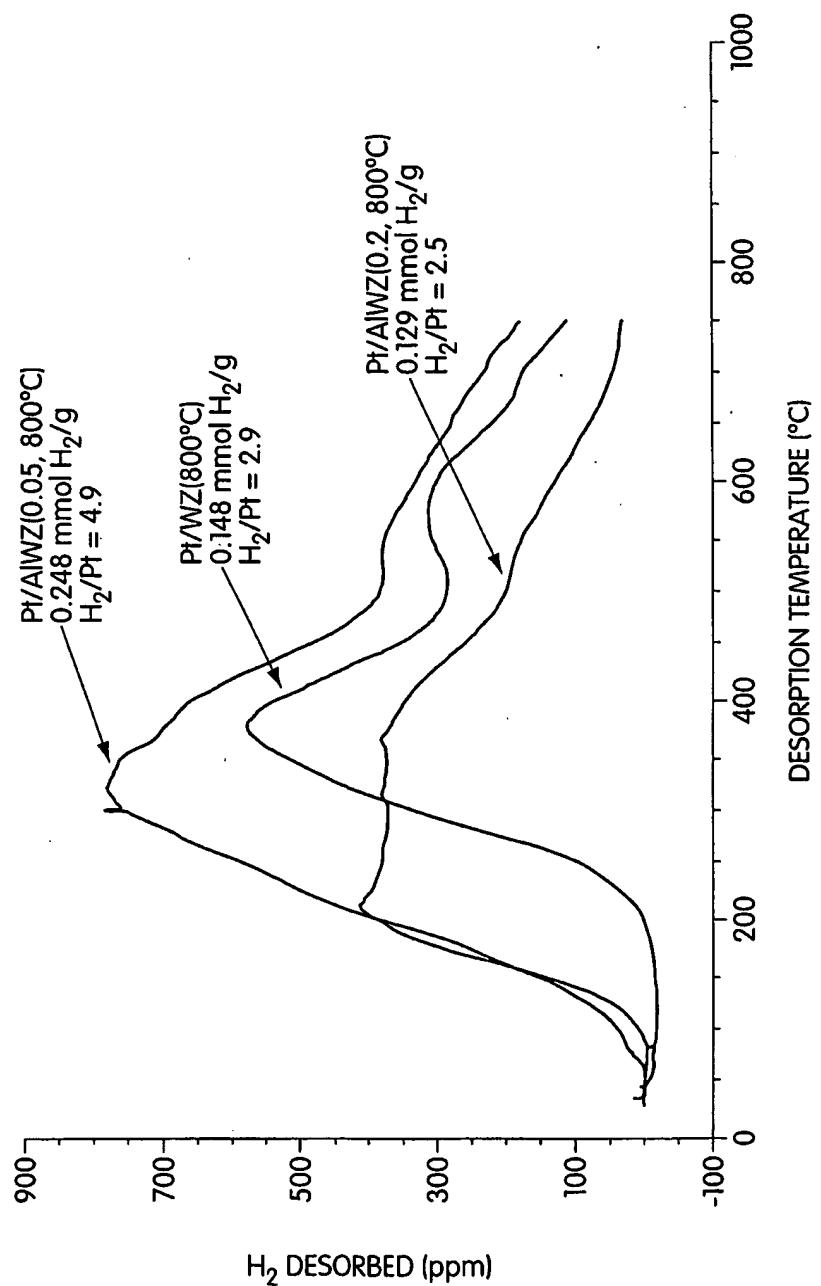


Fig. 13

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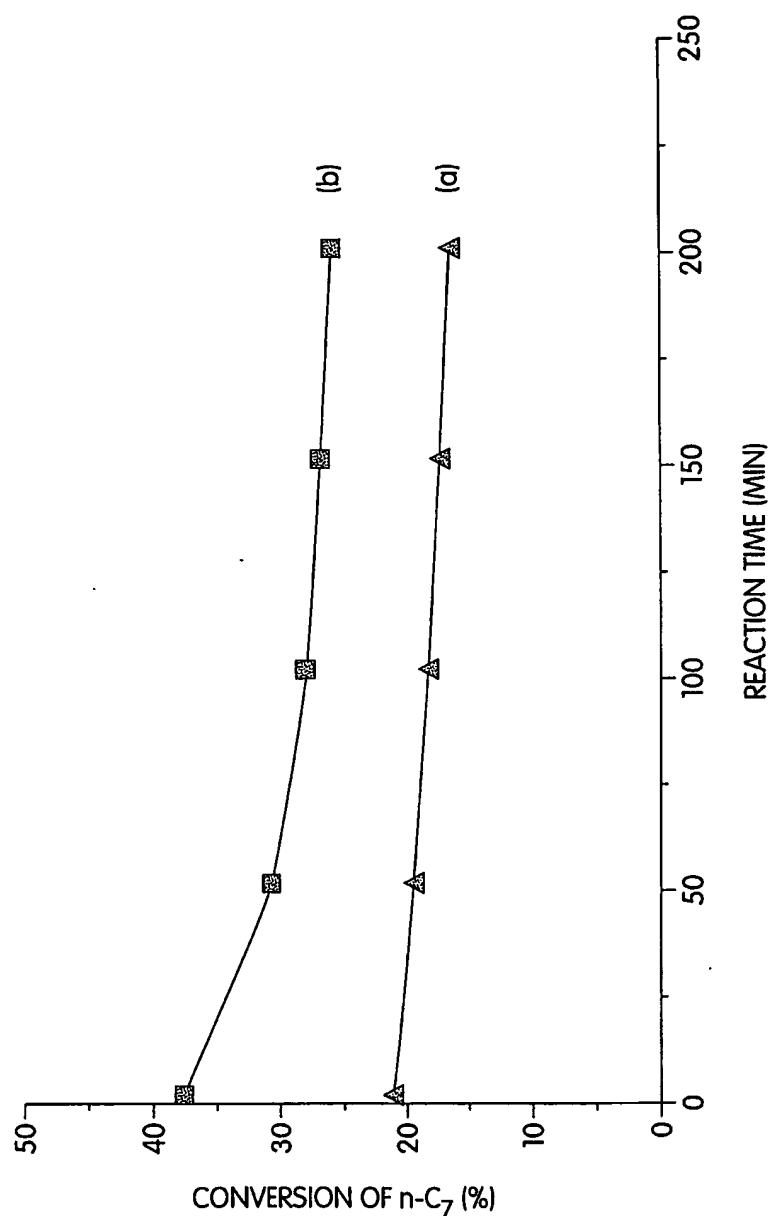


Fig. 15

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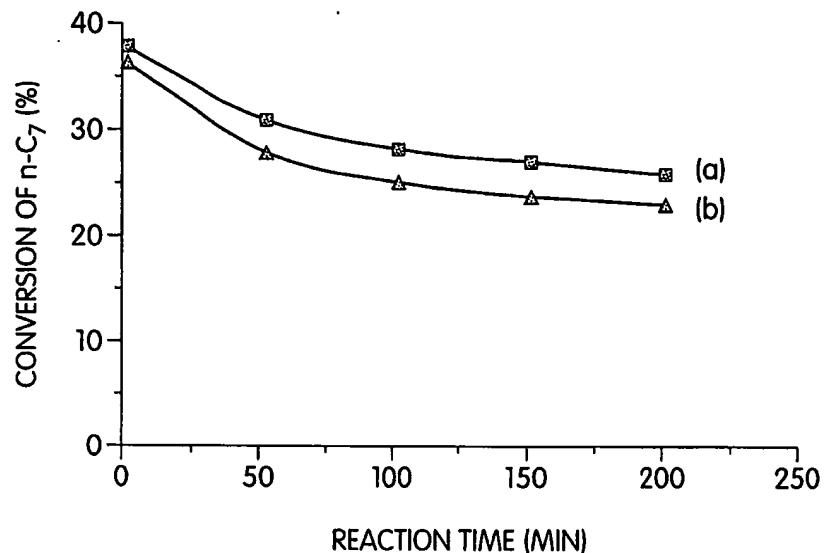


Fig. 16A

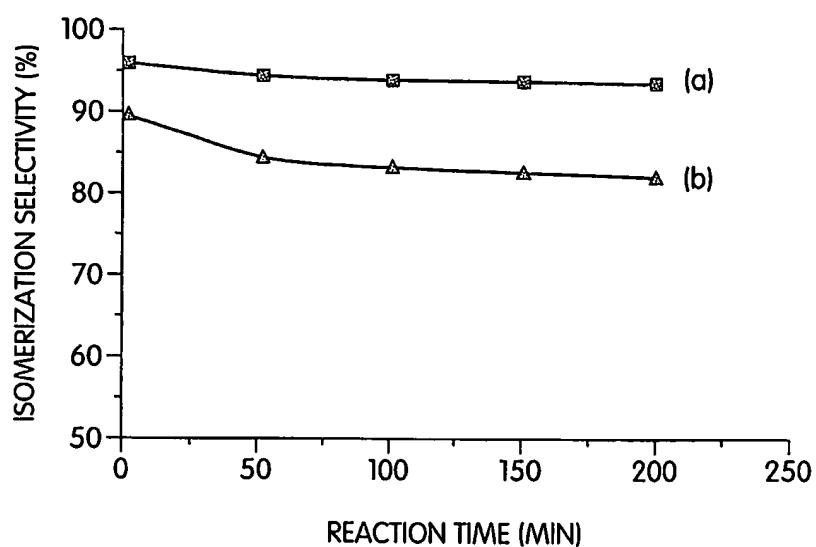


Fig. 16B

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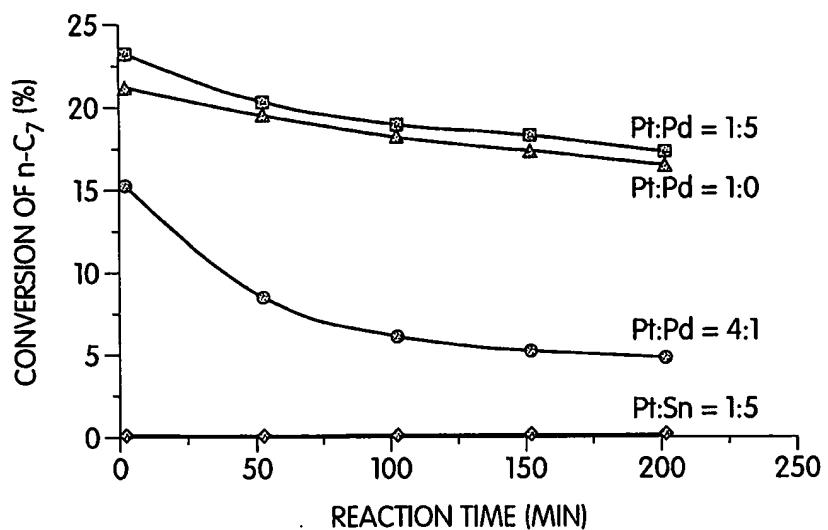


Fig. 17A

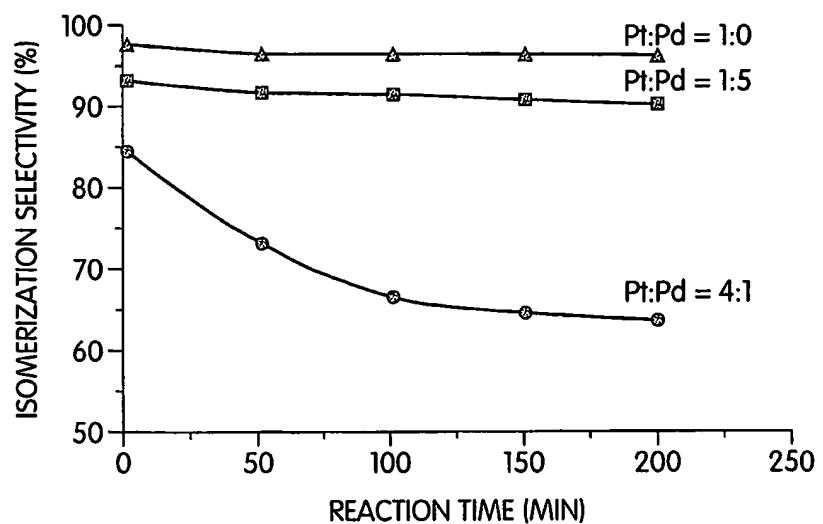


Fig. 17B

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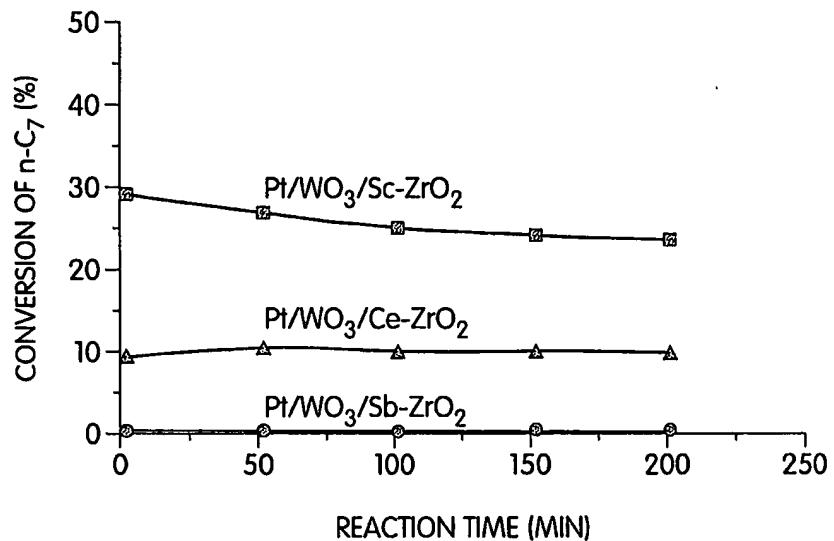


Fig. 18A

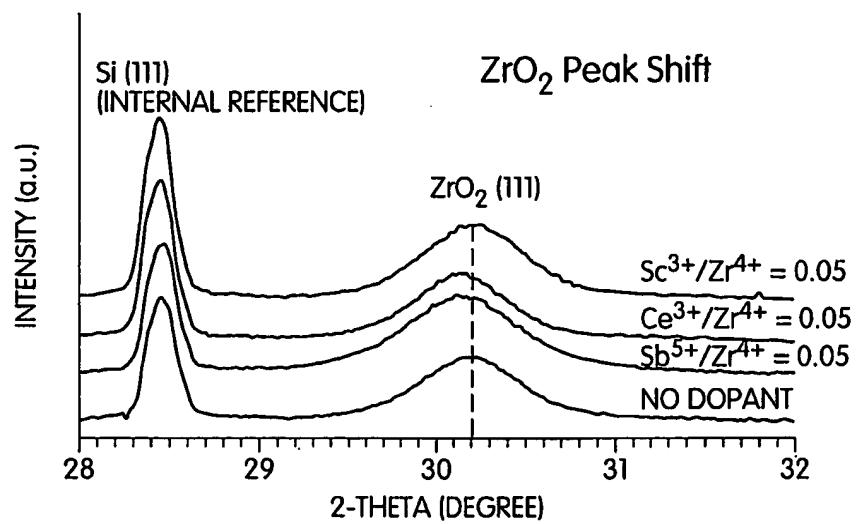


Fig. 18B

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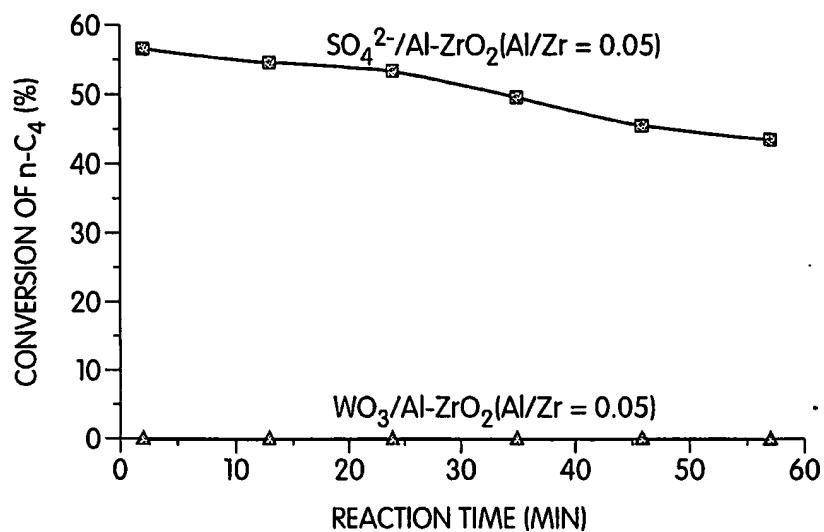


Fig. 19A

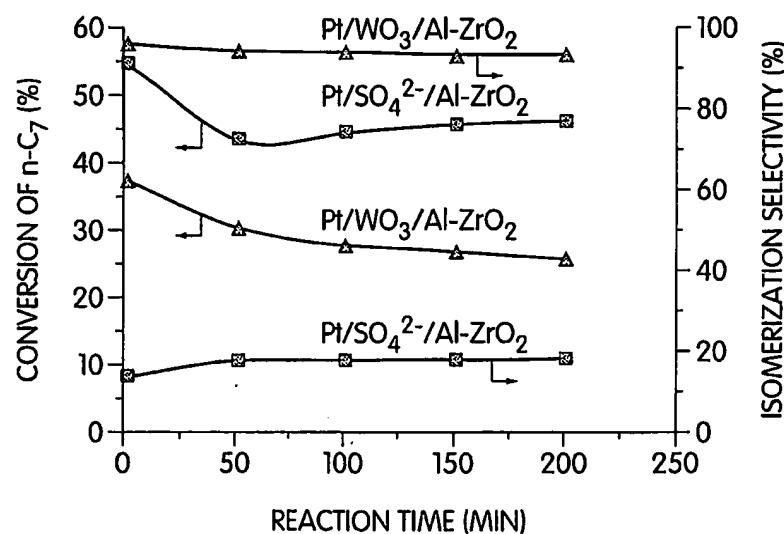


Fig. 19B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/25048

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01J 27/14, 27/186, 27/187, 27/199, 27/188, 27/19, 27/185, 27/02, 27/047, 27/051, 27/049, 27/045, 23/00
 US CL : 502/20/8, 210, 211, 213, 216, 219-221, 223, 305, 311, 313, 314, 316, 321, 322

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 U.S. : 502/20/8, 210, 211, 213, 216, 219-221, 223, 305, 311, 313, 314, 316, 321, 322

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,179,059 A (DOMESLE et al) 12 January 1993, column 2, line 10 to column 20, line 55.	1-15
A, P	US 6,316,381 B1 (AUER et al) 13 November 2001, column 2, line 12 to column 6, line 38.	1, 2, 4, 6, 8

<input type="checkbox"/>	Further documents are listed in the continuation of Box C.	<input type="checkbox"/>	See patent family annex.
*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report		
29 October 2002 (29.10.2002)	08 NOV 2002		
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Mark L. Bell Telephone No. 308-0661		